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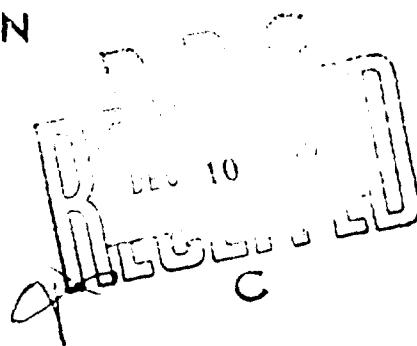
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IMPROVED MANGANESE PHOSPHATE COATINGS

HENRY CRAIN

APRIL 1975



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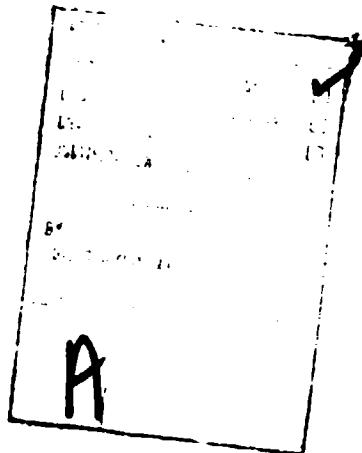
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to an exponential increase in the reaction rate constant with temperature for the conversion of manganese dihydrogen phosphate $[\text{Mn}(\text{H}_2\text{PO}_4)_2]$ to manganese phosphate $[\text{Mn}_3(\text{PO}_4)_2]$.



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TABULAR DATA

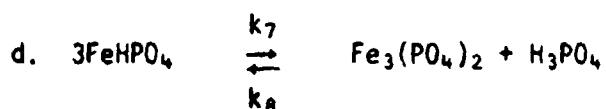
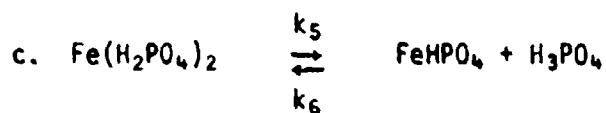
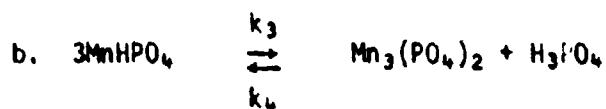
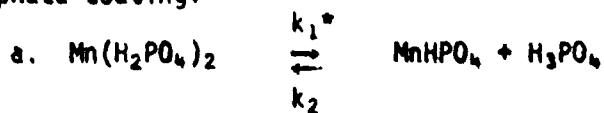
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INTRODUCTION

Manganese phosphate coatings have been applied to ferrous articles for more than sixty years. The coatings are simple to apply and offer an excellent base for oil or paint treatment. These coatings by themselves are required by specification MIL-P-16232 to withstand a 1-1/2 hour, 5 per cent salt spray test.

The conventional manganese phosphate bath contains manganese dihydrogen phosphate $[Mn(H_2PO_4)_2]$, ferrous iron (Fe^{++}), and phosphoric acid (H_3PO_4). The processing temperature range is usually $205^{\circ}F - 210^{\circ}F$. The base metal is pickled initially by the acid; hydrogen is liberated and consequently the pH of the solution is lowered at the metal-solution interface. The following hydrolytic reactions then occur to form the manganese and iron phosphate coating:



*k represents the reaction rate constant

Recently, a new and vastly improved manganese phosphate coating was produced in this laboratory. This new coating is formed by the addition of a metal-organic compound such as manganese tartrate, manganese gluconate, or manganese citrate to the conventional manganese phosphating bath and processing at temperatures in excess of $212^{\circ}F$. This coating is capable of withstanding more than a thousand hours in a 5 per cent salt spray test and exhibits the same remarkable corrosion resistance even after being subjected to a $450^{\circ}F$ heat treatment for one hour.

Several problems, however, have arisen in attempts to control the continuous reproduction of the superior coatings. To solve these problems required initiation of this study to obtain a better understanding of the underlying phenomena and reaction mechanisms of the modified manganese phosphating process.

PROCEDURE

The several phosphating baths that were used were of the following compositions:

- a. Manganese citrate bath - 10 grams/liter of manganese citrate was added to the conventional bath.
- b. Manganese tartrate bath - 10 grams/liter of manganese tartrate was added to the conventional bath.
- c. Iron-free bath - 20 grams/liter of manganese dihydrogen phosphate [$Mn(H_2PO_4)_2$] was added to deionized water. The free acid value was adjusted to 2.0 with phosphoric acid (H_3PO_4) and manganese carbonate ($MnCO_3$).
- d. Manganese dihydrogen phosphate bath - 10 grams/liter of $Mn(H_2PO_4)_2$ was added to the conventional bath.

All the above baths were operated at 213°F - 215°F. This temperature range was achieved by use of steam pressures less than one p.s.i.g. in an autoclave type processing vessel.

The specimens were mild steel panels measuring 2 by 3 by 1/16 inch. The specimens were degreased in trichloroethylene, abrasive-blasted with steel grit, and processed in the selected phosphating bath. Total immersion time for the processing of steel panels was 35 minutes.

The phosphate coating was stripped by a five-minute immersion in a solution of chromic acid heated to 200°F. The difference between the weight of the panel after processing and the weight after stripping gives the coating weight. The difference between the weight of the panel before processing and the weight after stripping yields the amount of iron etched.

Concentrations of the manganese and iron present in the bath, coating, and sludge were obtained by atomic absorption analysis. Titrations with sodium hydroxide were used to determine the free and total acid values.

Solubility studies were conducted in an attempt to measure the so-called "inverse solubility" of the phosphates. The filtered precipitate was dried and weighed from a known volume of phosphating solution that had been kept in an isothermal bath for a 30-minute period. The filtrate was then placed in an isothermal bath of higher temperature and the process outlined above was repeated. Additional solubility data were obtained with samples taken at regular temperature intervals from the processing autoclave, as the temperature was increased.

A study of pH at the metal-solution interface versus time of processing was attempted at various temperatures. In these experiments, a ball of degreased steel wool was wrapped around a hydrogen electrode, and the resulting pH was measured continuously on a recorder.

RESULTS

Various parameters of interest for the five types of phosphate baths used are summarized in Table I. The free and total acid values are approximately the same for the conventional manganese gluconate bath and for the manganese citrate bath. The $Mn(H_2PO_4)_2$ and iron-free baths have a higher total acid since an excess of $Mn(H_2PO_4)_2$ was added to the solution. The coating weights of the panels processed in baths containing some form of manganese enrichment are much greater than those panels processed in the conventional bath. The salt spray tests results show a five-hundred fold increase in corrosion resistance for these panels processed in a manganese-enriched bath as opposed to the conventional bath. The iron etched by pickling is also given in Table I.

Atomic absorption analyses of coatings, baths, and sludge to determine percentage manganese and iron are shown in Table II. Analyses of manganese citrate, tartrate, and gluconate sludges and coatings have been previously reported by Menke.¹ The manganese percentages for the coatings are very close to the calculated value of 46 percent for manganese in $Mn_3(PO_4)_2$. Percentages for the solutions are in weight percent and show a decrease in the manganese after each use of the processing solution. The insignificant amount of iron found in the coating of panels processed in the iron-free bath arises from the use of technical grade $Mn(H_2PO_4)_2$ and from the iron etched from the panels themselves.

¹ Menke, J., "A Study of Manganese Phosphating Reactions", Rodman Laboratory, Rock Island Arsenal Technical Report RE-TR-71-60, 1971.

TABLE I

Analyses of Solution and Coating for Phosphating
Baths of Differing Compositions

Bath type	Free acid in points NaOH*	Total acid in points NaOH*	Coating weight milligrams/square foot	Salt spray hours	Iron etched milligrams/panel
Conventional	4.0 maximum	24-27	1500	2	55
Manganese tartrate	2.5	30	7500	>1000	50
Manganese citrate	2.6	30	7500	>1000	60
Manganese dihydrogen phosphate	2.7	47	9000	>1000	45
Iron free	2.4	46	9200	>1000	45

*One point equals one milliliter of 0.1N NaOH per 10 milliliters of sample.

TABLE II

Atomic Absorption Analysis Results

	<u>Description of Sample</u>	<u>Percent Manganese by Weight</u>
A. <u>Sludges:</u>		
Conventional		12.5%
Manganese citrate		28.2%
Manganese dihydrogen phosphate		18.6%
B. <u>Coatings from:</u>		
Iron free bath (1st run)		39%
Iron free bath (2nd run)		37%
Iron free bath (3rd run)		46%
C. <u>Solutions:</u> Before and after processing.		
Iron free before	→ 1st run	0.65%
Iron free after		0.60%
Iron free before	→ 2nd run	0.68%
Iron free after		0.54%
Iron free before	→ 3rd run	0.62%
Iron free after		0.50%

Data for the solubility studies was difficult to obtain. In the study conducted by heating phosphate solutions in isothermal baths, a larger amount of precipitate was formed as the temperature of the bath was increased. However, the solubility was not only temperature-dependent but also time-dependent. Hence, even after the precipitate had been filtered from the solution, more formed because of the time dependency of precipitate formation. Atomic absorption analysis results for a solubility study that had been performed by the withdrawing of samples from the processing vessel at regular temperature intervals show an increase in precipitation with temperature (Table III). The largest increase in the amount of precipitate formed occurs between 200°F - 220°F.

A study of pH versus time of processing for various temperatures and additives was conducted to determine whether any relationship existed among these variables. Because of difficulties with the pH electrodes at the increased pressures, the results for temperatures above 210°F were impossible to obtain. For temperatures below 210°F, the plots varied slightly; but no definite relationships or trends could be established.

DISCUSSION

In the first experiments performed to produce superior corrosion resistant manganese phosphate coatings, manganese organic compounds were used. At that time, the beneficial effects of the manganese organic compounds were attributed to the organic part of the compound. The citrate, tartrate, and gluconate ions are well known for their chelating action; thus, investigators postulated that perhaps the manganese ion was held in solution by the chelate or combined with the iron to prevent its incorporation into the coating. Possible catalytic activity or buffering effects were also offered as explanations of the increased corrosion resistance. These experiments, however, indicate that the common factor for increased corrosion protection is manganese enrichment of the bath. All the baths that have yielded superior coatings have contained added amounts of manganese. Of more importance is the success of the conventional bath with 10 grams/liter of excess $Mn(H_2PO_4)_2$; thus, the complete absence of any chelating ion indicates that the concentration of manganese is extremely critical in the production of corrosion resistant coatings. For elimination of the presence of iron as a factor in phosphating, a bath containing only $Mn(H_2PO_4)_2$, H_3PO_4 , and deionized water was used. This bath produced four consecutive sets of phosphated panels that sustained salt spray tests for more than 1000 hours. The only intermittent addition made to the bath was manganese carbonate used to lower the free acid. The increase in manganese concentration permits more $Mn_3(PO_4)_2$ to be formed and, consequently, leads to a thicker, more protective coating. Because this coating is thicker, the amount of free pore area in the coating probably decreases so that less of the steel is exposed to corrosion.

TABLE III

Percentage by Weight of Manganese and Iron Present with
Increasing Temperature in a Phosphate Bath
Enriched with Manganese Tartrate

<u>Temperature</u>	<u>Percent Manganese</u>	<u>Percent Iron</u>
100°F	0.24	0.0034
200°F	0.23	0.0030
220°F	0.17	0.0027
240°F	0.14	0.0034
250°F	0.13	0.0029
260°F	0.12	0.0038
80°F*	0.18	0.0034

*stock bath unenriched

The other important factor necessary to produce superior phosphate coatings is that of a processing temperature above 212°F. Some investigators have used the term "inverse solubility" to explain the formation of more precipitate as the temperature is increased. However, the time dependency for precipitation, as shown in the solubility studies, indicates that the mechanism is a kinetic one rather than a solubility mechanism. The equation for a rate constant is given as:

$$k = Ae^{-E_a/RT}$$

where A = Constant

E_a = Energy of activation

T = Absolute temperature

R = Constant

As temperature increases, the rate constant will increase exponentially. Thus, for this particular phosphating system, the increase in temperature above 212°F becomes very important for the conversion of the soluble $Mn(H_2PO_4)_2$ to the insoluble $Mn_3(PO_4)_2$. The increase in $Mn_3(PO_4)_2$ formation produces thicker coatings and, consequently, less free pore area for corrosion sites.

CONCLUSIONS

- a. The manganese concentration in the phosphating solution is critical for producing coatings with superior corrosion resistance.
- b. The main function of the manganese organic compounds is to provide the bath with an increased manganese concentration.
- c. The exponential increase with temperature of the kinetic rate constant for the conversion of $Mn(H_2PO_4)_2$ to $Mn_3(PO_4)_2$ is an important factor for processing at temperatures higher than 212°F.

RECOMMENDATIONS

Further work should be conducted to determine:

- a. the critical manganese concentration needed to produce a superior coating,
- b. the differences in free pore areas that exist between conventional and Mn-enriched phosphate coatings, and
- c. a method to convert the $Mn_3(PO_4)_2$ sludge to the useful form of $Mn(H_2PO_4)_2$.

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